Accelerated Solvent Extraction for Sample Preparation of Chemical Weapon Degradation Compounds

Jay D. Sheffer, Spiros Z. Manolakos, and Donna E. Swartz

Constellation Technology Corporation

with support from the

Defense Threat Reduction Agency

Constellation Technology

DTRA
DEFENSE THREAT REDUCTION AGENCY

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2001		**00-00-2001 to 00-00-2001**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Accelerated Solvent Extraction for Sample Preparation of Chemical Weapon Degradation Compounds	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Constellation Technology Corporation,7887 Bryan Dairy Road Suite 100,Largo,FL,33777**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT
see report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**		**19**	

Background

- **Analytical methods are needed for the monitoring of chemical weapons (CW) under the Chemical Weapons Convention**
- **One approach involves the detection of degradation compounds that remain following exposure of CW agents to the environment**
- **However, time is severely limited for conducting on-site analyses, therefore instrumentation which performs fast soil extractions and analyses is of great interest to those performing such analyses**

Scope of Work

Assess the feasibility of employing an Accelerated Solvent Extraction (ASE) system to selectively extract CW degradation compounds from environmental samples (soils) for determinative chemical analysis

- Develop and implement method for derivitization and characterization of CW degradation compounds via gas chromatography-mass spectrometry (GC-MS)
- Optimize ASE experimental parameters for extraction of CW degradation compounds spiked onto characterized soils and determine overall performance

Target Compounds

Compound Name	Abbreviation	CW Source
Thiodiglycol sulfone	TDGS	Mustards
Thiodiglycol	TDG	Mustards
Ethylmethyl phosphonic acid	EMPA	Sarin, Soman, VX
Methyl phosphonic acid	MPA	Sarin, Soman
Pinacolylmethyl phosphonic acid	PMPA	Soman
Ethylmethyl phosphonothioic acid	EMPTA	VX
Diisopropylamino ethanol	DIPAE	VX
Triethanol amine	TEA	Mustards

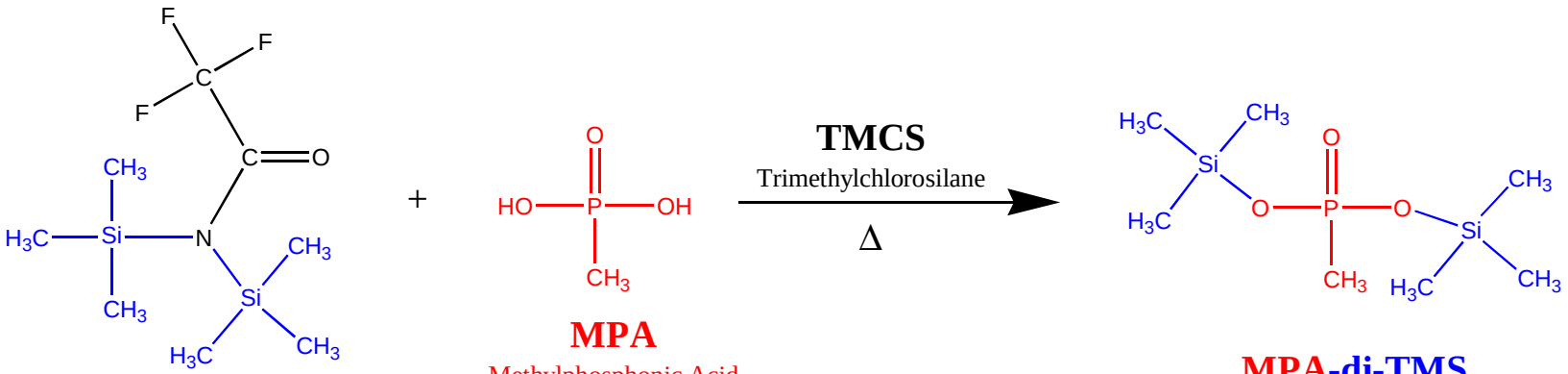
GC-MS Characterization

- **Implement instrument operating method using ROP* as a guide**
  - Establish sample prep and derivitization procedures
  - Develop method for quantitative analysis of target compounds following ASE extraction

***Recommended Operating Procedure (ROP) for On-Site Analysis by Gas Chromatography - Mass Spectrometry**
(Version 2.0 of Report of the Specialist Task Force on Analytical Issues to the Expert Group on Inspection Procedures (13.06.1996)

Derivitization of Target Compounds

Target compounds cannot be detected directly by GC-MS; they must be derivitized by BSTFA prior to GC-MS analysis



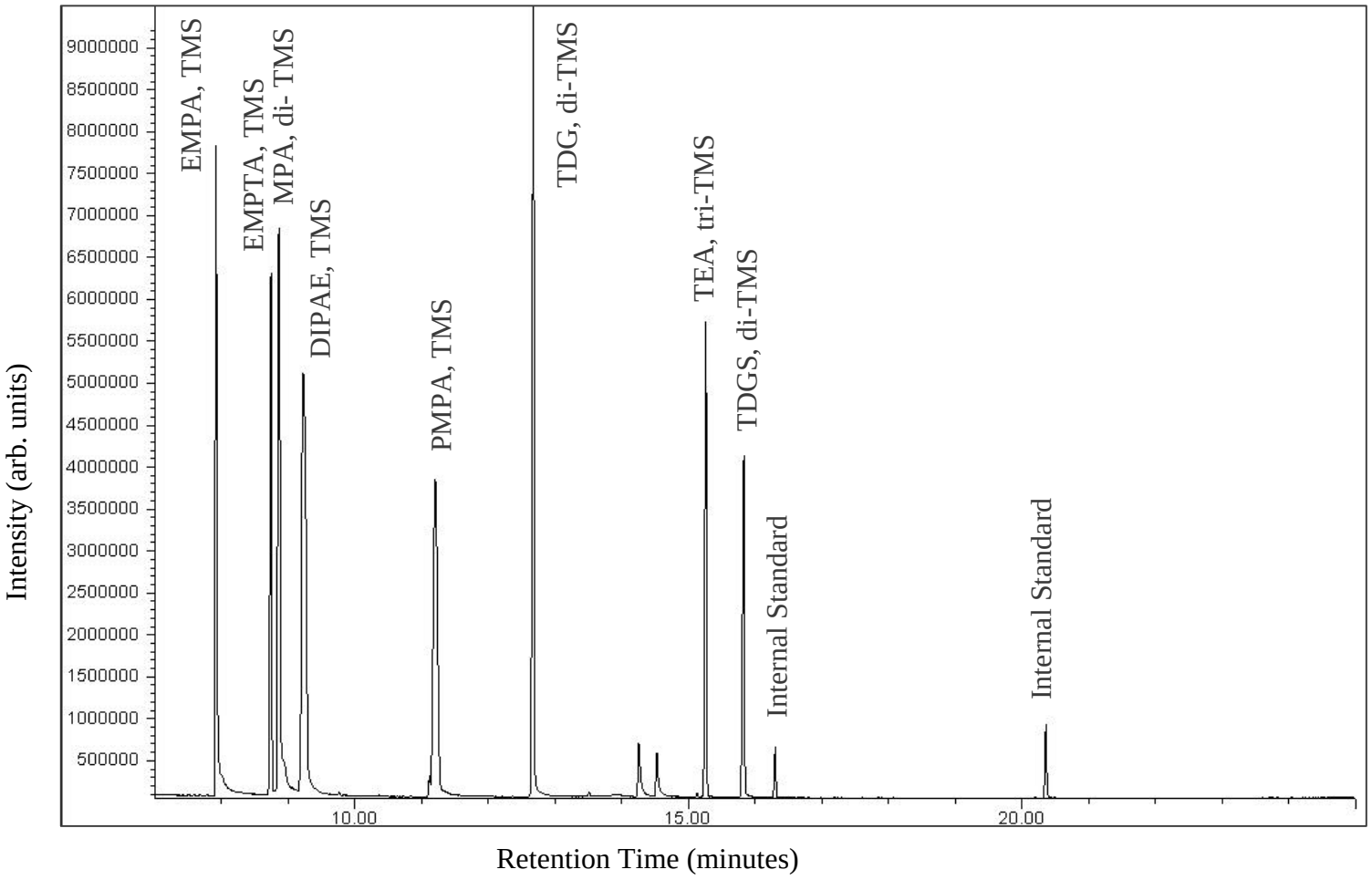
BSTFA
2,2,2-trifluoro-N,N
-bis(trimethylsilyl)-acetamide

MPA
Methylphosphonic Acid

MPA-di-TMS
Methylphosphonic acid, TMS derivative

Total Ion Chromatogram

Derivitization and separation of all 8 target compounds



Principles of ASE

Accelerated Solvent Extraction is accomplished by applying high pressure and temperature to an extraction cell containing the sample and solvent

- High temperature = greater solubility and solvent capacity, increased migration rate of analyte
- High pressure maintained to keep solvent in liquid phase at high temperatures

Dionex ASE® 200 Schematic

#1 Load sample into cell.

#2 Fill cell with solvent and heat. (Solvent, volume, Temp.)

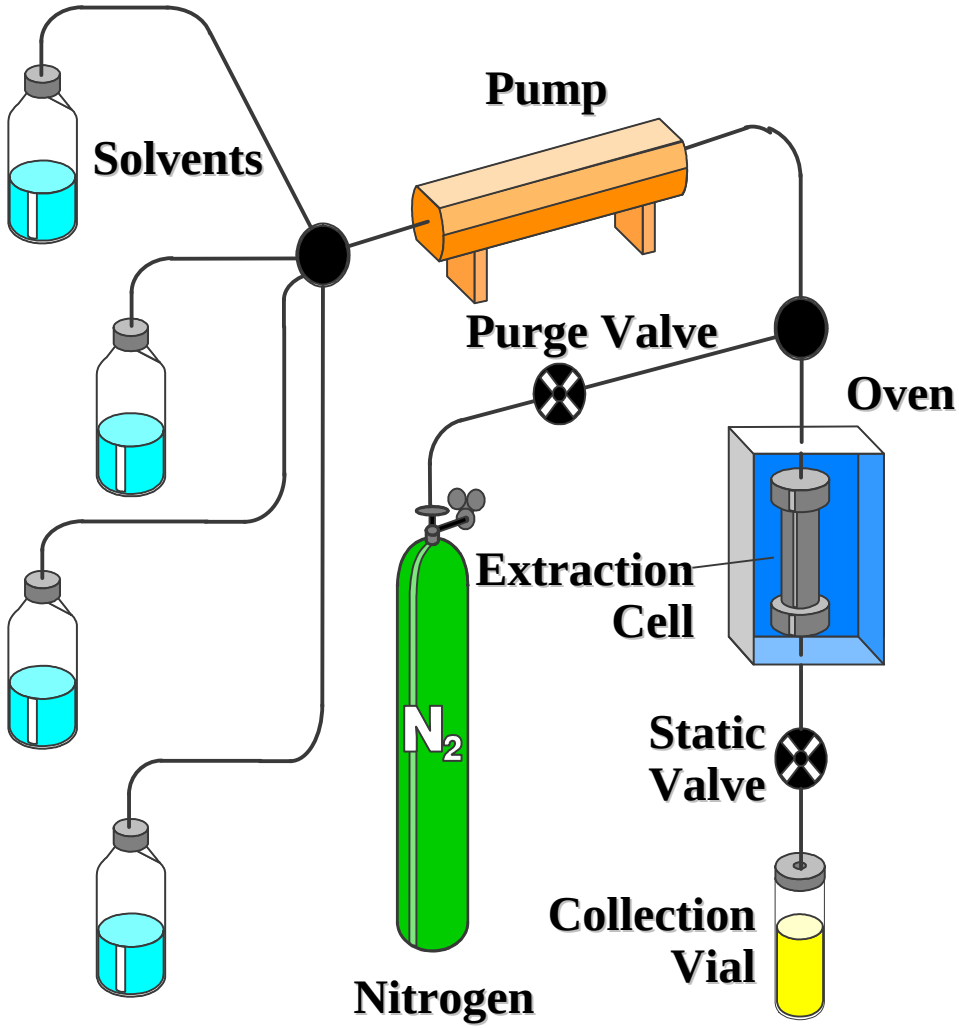
#3 Pressurize cell. (1500psi)

#4 Hold sample at pressure and temperature. (Static time)

#5 Pump clean solvent into sample cell. (Flush volume)

#6 Purge solvent from cell with N_2 gas.

#7 Extract ready for analysis.



ASE Instrument Parameters

Parameters	Experimental Values
• Solvent	Methanol
• Solvent Temperature	100 ºC - 200 ºC
• Solvent Flush Volume	60% of 22 mL Extraction Cell
• Static (Extraction) Time	5 minutes
• Number of Static Cycles	1 cycle
• Cell Pressure	1500 psi

Experimental Procedure

- **Characterized soils obtained from R.T. Corporation**
  - Soil #1 - sandy loam
  - Soil #2 - sandy clay-loam
  - Soil #3 - loam
  - Inert Sand (Ottawa Sand,20 - 30 mesh: Fisher Scientific)
- **Soils spiked with ~ 500mg target compound per 10g of soil prior to ASE extraction (50ppm target/10g soil)**
- **Optimize ASE instrument parameters (mainly temperature) by determining percent recoveries of analytes**

Experimental Procedure

- **ASE extractions performed in sets of 12, 3 cells for each soil matrix, for each of the 8 target compounds and using extraction temperatures of 100°C, 125 °C, 150 °C, 175 °C, and 200 °C……480 extractions!**

  ⇒ Time required for extraction of 24 samples: 6 - 8 hours + sample prep time (loading and cleaning of extraction cells, etc.)

Experimental Procedure

- **Evaporation of solvent by nitrogen blowdown**
- **Derivitization of extracted target compounds**

  ⇒ Time required for solvent evaporation and derivitization: 6 - 8 hours

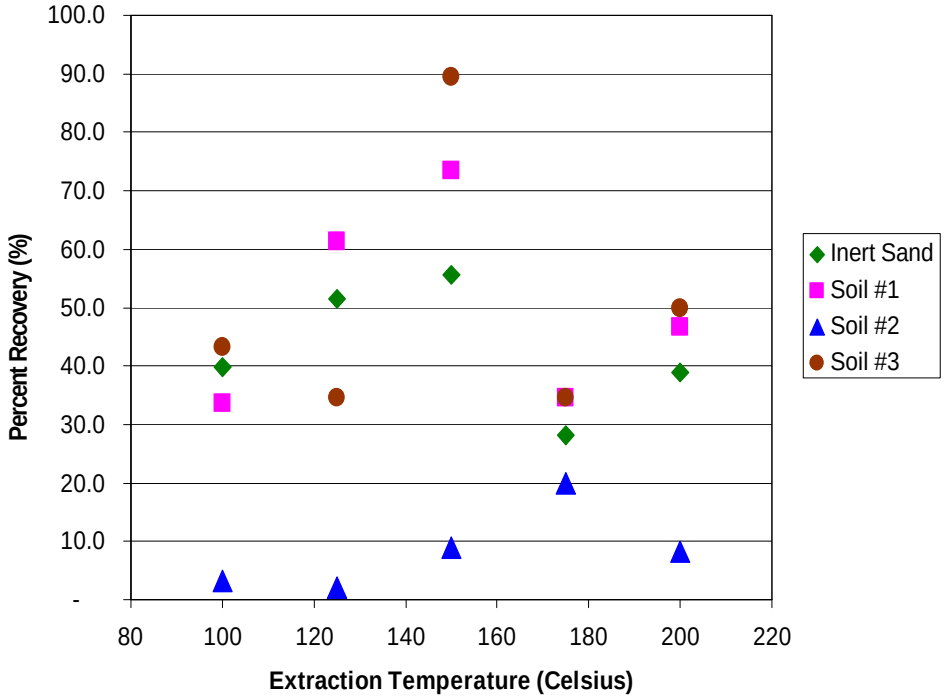
- **Dilution of derivitized samples and addition of internal standards followed by GC-MS analysis**

  ⇒ Time required for GC-MS analysis of 30 samples (24 ASE extractions + 6 daily QC samples): 24 hours

Percent Recoveries

- Example of data generated for one of the 8 target compounds; each data point is the average of 3 identical runs

TDG



	100 ℃	125 ℃	150 ℃	175 ℃	200 ℃
Inert Sand	39.8 ± 2.9	51.4 ± 2.1	55.7 ± 6.6	28.1 ± 2.9	38.9 ± 14.3
Soil #1	33.6 ± 3.6	61.4 ± 19.1	73.5 ± 17.1	34.6 ± 5.8	46.7 ± 3.1
Soil #2	3.1 ± 2.8	2.1 ± 3.6	8.9 ± 13.4	19.8 ± 20.1	8.2 ± 7.1
Soil #3	43.2 ± 7.7	34.6 ± 30.4	89.4 ± 9.8	34.5 ± 6.6	49.9 ± 7.7

Maximum Recoveries of Target Compounds Using ASE

	Inert Sand	Soil #1 Sandy Loam	Soil #2 Sandy Clay-Loam	Soil #3 Loam
TDG	56 ± 7 %	74 ± 17 %	8 ± 7 %	89 ± 10 %
TDGS	99 ± 3 %	95 ± 19 %	1 ± 1 %	77 ± 1 %
EMPTA	95 ± 9 %	57 ± 7 %	4 ± 2 %	42 ± 2 %
PMPA	40 ± 4 %	30 ± 3 %	1 ± 1 %	6 ± 2 %
EMPA	28 ± 2 %	14 ± 1 %	1 ± 1 %	4 ± 2 %
MPA	2 ± 2 %	0 %	0 %	0 %
DIPAE	74 ± 10 %	23 ± 3 %	5 ± 4 %	14 ± 3 %
TEA	60 ± 4 %	2 ± 2 %	2 ± 2 %	4 ± 0 %

CONCLUSIONS

- **Highest recoveries obtained at 100°C to 150°C**
- **High extraction temperatures (175°C and 200°C) yield lower recoveries, possibly due to:**

  ⇒ Greater extraction of interfering organic compounds

  ⇒ Breakdown of target compounds
- **Poor recoveries in Soil #2, possibly due to smaller particle size (greater surface area)**
- **Inert sand and Soil #1 yield highest recoveries**

CONCLUSIONS

With the exception of Soil #2…

- **Excellent recovery of TDG, TDGS, EMPTA (50 - 90%)**
- **Moderate recovery of EMPA, TEA, DIPAE in sand (25 - 50%), poor recovery in soil #1, #3**
- **Moderate recovery of PMPA in sand, soil #1 (30 - 40%), poor recovery in soil #3**
- **Poor recovery of MPA in all matrices (< 10%)**

Evaluation of ASE for CW Sample Prep

- **Advantages of ASE for CW Sample Prep**
  - Automation of solvent extraction
  - Fast extraction time
  - Low volumes of solvent used
  - High recoveries of TDG, TDGS, and EMPTA

- **Disadvantages of ASE for CW Sample Prep**
  - Cost of equipment and maintenance required after 100's of extractions
  - Moderate recoveries of EMPA, PMPA, TEA, DIPAE in inert sand only
  - Poor recovery of MPA in all matrices
  - Poor recoveries of all analytes from soil #2

Future Work

- **Investigate "fast" GC technology to reduce GC-MS analysis time and increase sample throughput**
- **Equipment to be used:**

  Agilent Tech. 6890 fast GC equipped with an O.I. Analytical pulsed-flame photometric detector (PFPD) or an Agilent 5973 mass-selective detector